



Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents

P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira *

Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

The application of catalytic ozonation processes for the decolourisation and mineralisation of coloured aqueous solutions was studied. One acid azo dye, CI Acid Blue 113, and two reactive dyes, CI Reactive Yellow 3 and CI Reactive Blue 5, with azo and anthraquinone chromophores, respectively, were used as representative textile dyes. The catalytic activities of activated carbon, cerium oxide and a ceria-activated carbon composite were evaluated in the removal of the selected dyes. In all cases, with an initial dye concentration of 50 mg/L, a complete decolourisation was achieved by single ozonation in short reaction times (less than 10 min). The ceria-activated carbon composite allowed the highest removal of total organic carbon. For dye concentrations of 50 mg/L, mineralisation degrees of 100%, 98% and 97% were achieved with the composite after 2 h of reaction, respectively for CI Reactive Blue 5, CI Acid Blue 113 and CI Reactive Yellow 3. The activity of the catalyst containing cerium was affected by the presence of carbonate and bicarbonate ions due to their scavenging effect towards hydroxyl radicals; for example the mineralisation degree of CI Reactive Blue 5 ($C_0 = 300$ mg/L) after 120 min of reaction was only 63%, contrasting with the value of 85% obtained in the absence of carbonates. All the catalytic systems were evaluated in the treatment of textile effluents, collected before or after conventional biological treatment. Catalytic ozonation was proven to be effective when used as tertiary treatment for bio-treated effluents.

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1. Introduction

Intense colour is one of the main characteristics of textile wastewater originated from spent dye baths and dye rinsing operations. Besides the undesirable aesthetic impact caused by such effluents in receiving natural water courses, the persisting colour and the non-biodegradable nature of most of the textile dyes represent serious problems to the environment [1]. Conventional aerobic biological treatments have proven insufficient to completely remove colour from textile plant effluents [2,3]. Although there are several physical-chemical methods applied for colour removal, such as adsorption, membrane processes or physico-chemical treatments, chemical oxidation has become the method of choice due to its high efficiency and ease of operation. Ozonation of textile wastewater, spent and simulated dye baths has been focus of investigation [4–7]. Owing to its extremely high redox potential ($E^0 = 2.07$ V), ozone is one of the most effective oxidant agents used for this purpose. It reacts selectively with

aromatic and unsaturated moieties [8], such as the chromophore structures of dye molecules, leading to fast decolourisation of the solutions. However, depending on the operational conditions and the nature of pollutants, the extent of mineralisation is usually insufficient. The oxidation of dyes and chemical auxiliaries present in textile effluents leads to the formation of intermediates that are frequently resistant to ozone attack. Such compounds of low reactivity towards ozone may be efficiently removed by oxidation via HO^\bullet radicals [8]. Presently, advanced oxidation processes and catalytic oxidation are the main emerging routes for the removal of such compounds.

In order to enhance the efficiency of the ozonation processes, methods combining ozone with hydrogen peroxide, UV radiation, metallic ions or heterogeneous catalysts have been subject of intense research [9]. Heterogeneous catalytic ozonation aims to enhance the removal of more refractory compounds by the transformation of ozone into more reactive species and/or by adsorption and reaction of the pollutants on the surface of the catalyst [10]. Oxides of transition metals are trendy catalysts in ozonation processes [11–14], and activated carbon is also an attractive and promising alternative to the treatment of wastewater containing dyes or other organic contaminants [15–23]. In spite of the intense research, the development of highly effective

* Corresponding author. Tel.: +351 225081468; fax: +351 225081449.

E-mail addresses: pfaria@fe.up.pt (P.C.C. Faria), jjmo@fe.up.pt (J.J.M. Órfão), fpereira@fe.up.pt (M.F.R. Pereira).

catalysts for the application in ozonation processes, and the understanding of the inherent mechanisms are of great relevance.

In our previous research [24,25], the incorporation of cerium oxide and activated carbon was shown to be highly effective in the catalytic ozonation of a series of organic compounds. Experiments carried out in the presence of the radical scavenger *tert*-butanol supported the involvement of hydroxyl radicals (HO^\bullet) in the oxidation mechanism.

The present work reports data on the catalytic ozonation of three commercial dyes from different chemical classes and distinct applications. One acid azo dye, CI Acid Blue 113 (AB113), and two reactive dyes, CI Reactive Yellow 3 (RY3) and CI Reactive Blue 5 (RB5), with azo and anthraquinone chromophores, respectively, were used as representative dyes. The effect of the dye concentration and the presence of bicarbonate (HCO_3^-) and/or carbonate (CO_3^{2-}) ions was assessed in non-catalytic and catalytic ozonation of RB5. With the main goal of validating the results obtained with the synthetic solutions, two textile effluents were used as case studies. The first one was collected after a conventional aerobic biological treatment. The second one is a global raw textile effluent collected in a dyeing mill, at the homogenisation tank.

Three different materials, activated carbon (AC_0), cerium oxide (Ce-O), and a composite of activated carbon and cerium oxide ($\text{AC}_0\text{-Ce-O}$) were assessed. The performance of the catalytic systems was evaluated in terms of the decolourisation of the solutions and, mostly, in terms of the extent of mineralisation achieved, since this is an important parameter when evaluating the effectiveness of a given wastewater treatment.

2. Experimental

2.1. Materials

In the present experimental study the synthetic coloured effluents were simulated considering three dyes belonging to different chemical classes: CI Acid Blue 113 (AB113), CI Reactive Yellow 3 (RY3) and CI Reactive Blue 5 (RB5). The molecules of the first two dyes have azo chromophores, while the latter possesses an anthraquinone chromophore group (Table 1). Regarding their application, the reactive dyes are used mostly in the dyeing of cellulosic fibres, and represent one of the most used classes of dyes. These dyes contain a reactive group, either a haloheterocycle, such as chlorotriazine, or an activated double bond, for instance of the

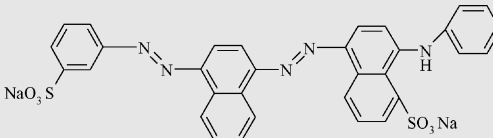
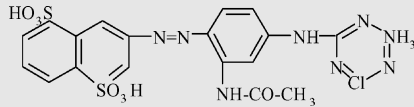
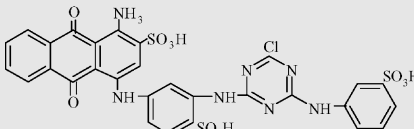
vinylsulfone type, which forms chemical bonds with hydroxyl groups of the cellulosic fibres, when applied in alkaline medium. Reactive dyes have a low fixation degree compared to other types of dyestuff, since the functional group also bonds to water, becoming hydrolyzed, therefore inhibiting the reaction with the fibre [26,27]. Acid dyes are normally used for dyeing wool, silk and some synthetic fibres such as nylon. The corresponding molecules usually have a sulfonic or amino group that makes them soluble in water. These dyes are normally available as the corresponding sodium salts and, therefore, they are anionic in solution.

Two different textile effluents were assessed in this study. Textile effluent A (TEA) was collected in a collective wastewater plant, after conventional activated sludge treatment, but before the subsequent physical-chemical step. Therefore, it is representative of a global bio-treated textile wastewater. Textile effluent B (TEB) results from the mixture of all the liquid effluents produced in a textile dyeing mill. The main characteristics of each effluent will be presented in Section 3.2. Before the ozonation experiments both samples were filtered under vacuum in order to remove suspended solids.

The preparation and characterization of the catalysts selected for this study (AC_0 , Ce-O and $\text{AC}_0\text{-Ce-O}$) have already been presented and are described elsewhere [25,28]. Briefly, the cerium oxide catalyst (sample Ce-O) was prepared by precipitation, according to the procedure described by Imamura et al. [29], using aqueous solutions of cerium (III) nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL H_2O) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at 100 °C for 24 h and calcinated in air ($50 \text{ cm}^3 \text{ min}^{-1}$, measured at room T and P) at 450 °C for 3 h. A composite of activated carbon and cerium oxide (sample $\text{AC}_0\text{-Ce-O}$) was prepared by a similar procedure as for sample Ce-O , where a given amount of activated carbon was dispersed in the nitrate solution before addition of NaOH. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was used as received. After precipitation, the suspension was shaken for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at 100 °C. This material was calcinated at 450 °C for 3 h under a flow of N_2 ($50 \text{ cm}^3 \text{ min}^{-1}$, measured at room T and P). The catalysts were sieved to a particle size of 100–300 μm prior to reaction studies.

Thermal analysis of sample $\text{AC}_0\text{-Ce-O}$, carried out in a Mettler TA 4000 thermal analyser under a flow of air, revealed a cerium

Table 1
Properties of the selected dyes.

Generic name (commercial name)	Molecular structure	Chemical class	λ_{max} (nm)
CI Acid Blue 113 (Erionyl Navy R)		Azo	566
CI Reactive Yellow 3 (Cibacron Yellow R)		Azo	411
CI Reactive Blue 5 (Cibacron Blue BR)		Anthraquinone	598

oxide average content of 45 wt%. Samples Ce-O and AC₀-Ce-O have BET surface areas of 72 and 583 m²/g, respectively. The selected activated carbon is an acid washed granular activated carbon (particle size of 0.42–2 mm) produced by steam activation of selected grades of coal, it has a BET surface area of 909 m²/g, a mesopores surface area of 100 m²/g, a micropore volume of 0.332 cm³/g, a pH_{PZC} of 8.5, and its complete characterization is reported elsewhere [15,28]. According to the XRD results, the dominant diffraction peaks observed for both ceria-containing samples are those characteristic of cerianite (CeO₂) (JCPDS #43–1002). The presence of the Ce (IV)/Ce (III) redox couple on the surface of the catalysts was evidenced by XPS analysis. Additional detailed information on the characterization of the ceria-based materials is reported elsewhere [25].

2.2. Kinetic experiments and analytical methods

The removal of AB113, RY3 and RB5 from aqueous solutions was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket (see Fig. 1). Ozonation experiments in the absence of catalyst, and adsorption on activated carbon were performed in the same system, under identical experimental conditions. The synthetic coloured solutions were prepared by dissolving the desired amount of dye in distilled water. In every experiment the reactor was filled with 700 mL of each dye solution at a given concentration (50 or 300 mg/L), and at its natural pH (5–6). In the adsorption and catalytic ozonation experiments, 350 mg of catalyst (particle size = 100–300 µm) were used. The temperature of the reactor was maintained at 25 °C. The experiments were carried out at constant gas flow rate (150 cm³/min, measured at room T and P) and constant inlet ozone concentration (50 g/Nm³). Additional experimental conditions and procedures are reported elsewhere [23]. The textile effluents were submitted to non-catalytic and catalytic ozonation under similar operational conditions.

The concentrations of each dye in the solutions were followed by UV–vis spectrophotometry with a JASCO V-560 UV/Vis spectrophotometer. The UV–vis spectra were measured at given

time intervals. The degree of mineralisation was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer. In selected experiments, HPLC analyses were performed using a Hitachi Elite Lachrom HPLC equipped with a diode array detector, in an attempt of identifying the final oxidation by-products. The stationary phase was an YMC Hydrosphere C18 column (250 mm × 4.6 mm) working at room temperature under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2.0.

Repetitions of selected experiments were carried out and the results were found to be reproducible with a maximum error of ca. 3% in % TOC removal relatively to the average.

3. Results and discussion

3.1. Mineralisation of synthetic coloured solutions

The mineralisation of the AB113, RY3, and RB5 solutions with an initial concentration of 50 mg/L was carried out by ozonation catalysed by AC₀, Ce-O and AC₀-Ce-O. Blank experiments of non-catalytic ozonation (ozonation process alone) and adsorption on activated carbon were carried out for comparative purposes.

Non-catalytic ozonation is a powerful process for the degradation of dyes since ozone has the ability to selectively react with their chromophores, leading to high and fast colour removal. In the present work, all the dye solutions were effectively decolourised after very short reaction periods. In order to clarify the changes in the molecular and structural characteristics of the species resultant from the ozonation, the evolution of the UV–vis spectra of each dye solution was recorded, as a function of time, and are depicted in Fig. 2.

The absorption spectra of AB113, RY3 and RB5 are characterized by one main band in the visible region, with the maximum absorption at 566, 411 and 598 nm, respectively, which is associated with the chromophores of the dye molecules. The evolution of the UV–vis spectra during non-catalytic ozonation followed a similar trend for all dyes, i.e. the spectrum of each dye solution changes along time, with the disappearance of the band in the visible region, due to the ozone attack on the chromophore

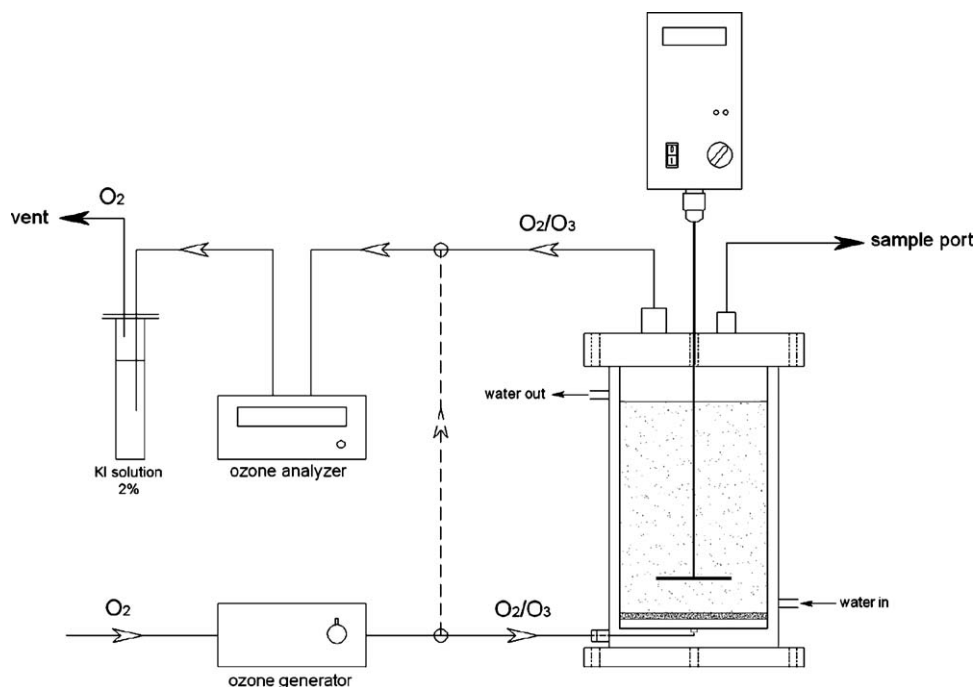


Fig. 1. Schematic representation of the experimental set-up.

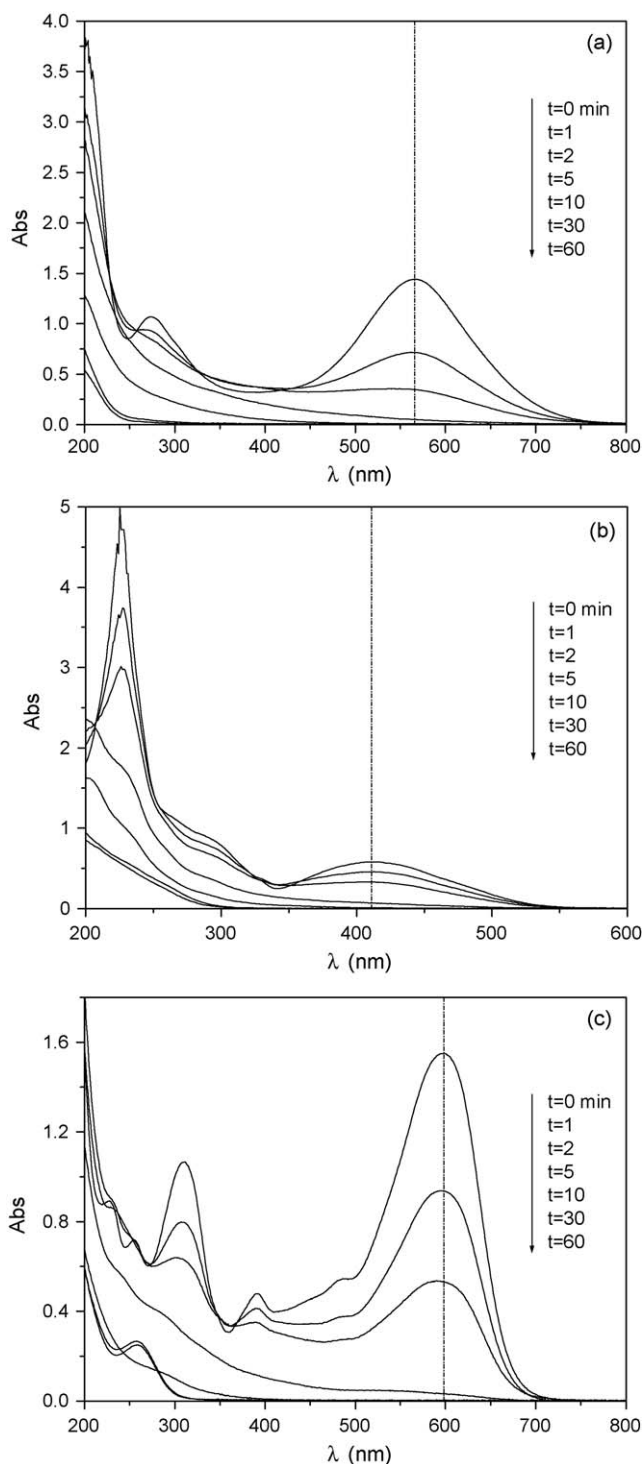


Fig. 2. Evolution of UV-vis spectra of (a) CI AB113, (b) CI RY3 and (c) CI RB5 during non-catalytic ozonation ($C_0 = 50$ mg/L).

group, which determines the colour disappearance of the solution. In addition to the rapid bleaching effect, the decay of the absorbances in the UV region is considered an evidence of the degradation of the aromatic fragments of the dye molecules and their oxidation intermediates. Particularly, the absorbance at 254 nm is commonly associated with the presence of aromatic moieties.

The UV-vis spectra recorded in the early stages of the catalytic ozonation of each dye are coincident, in all cases, with those

obtained during non-catalytic ozonation. The decolourisation of the solutions during ozonation occurs mainly through the direct attack of ozone to the chromophore groups of the dye. This reaction is very fast and selective and, therefore, no major enhancements are achieved with the catalytic ozonation, concerning the decolourisation step (results not shown).

Experimental data corresponding to the decolourisation kinetics of AB113, RY3 and RB5 by non-catalytic ozonation and adsorption on AC_0 are depicted in Fig. 3, in order to allow the comparison of the performance of the different dyes towards activated carbon adsorption and ozone attack. The colour of the solutions was assessed at the wavelength corresponding to the maximum absorption in the visible region of the UV-vis spectrum of each dye (see Table 1).

Under the experimental conditions used in this work, the adsorption of the selected dyes is rather limited, as shown in Fig. 3. In fact, the RY3 dye has a very low affinity towards activated carbon. After 120 min, the removal of AB113 and RB5 by adsorption on AC_0 was ca. 18% and 11%, respectively. These values are in agreement, within the experimental error, with those obtained in the TOC measurements. The presented data show that adsorption is not effective for the decolourisation of these solutions. On the other hand, single ozonation allows a fast colour removal in short reaction times (less than 10 min). Comparing the experimental data corresponding to the colour removal kinetics of the three dyes, it was observed that the decolourisation rate of RY3 was inferior to that of AB113 or RB5. After 5 min of single ozonation the colour removal obtained for the solutions of AB113, RY3 and RB5 was ca. 97%, 88% and 98%, respectively. During this period, the colour removal achieved by adsorption on AC_0 varied between less than 1% for RY3 and 7% for AB113. Consequently, the contribution of the adsorption on activated carbon to the decolourisation step during the ozonation catalysed by AC_0 may be considered negligible.

Nevertheless, activated carbon is expected to play an important role in the adsorption of some reaction intermediates as well as in catalysing their oxidation, as it will be discussed later. The ozonation of the coloured solutions leads to the fragmentation of the dye molecules into smaller organic compounds that remain in the solution for further oxidation. When comparing the results obtained for the mineralisation of the solutions, it was found that

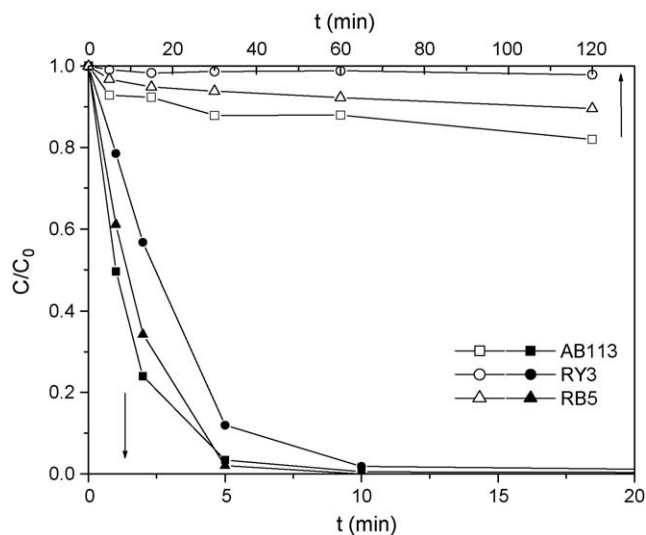


Fig. 3. Kinetics of decolourisation by non-catalytic ozonation (filled symbols) and adsorption on AC_0 (open symbols) of AB113, RY3 and RB5 at the natural pH of the solutions ($C_0 = 50$ mg/L, $AC_0 = 0.5$ g/L).

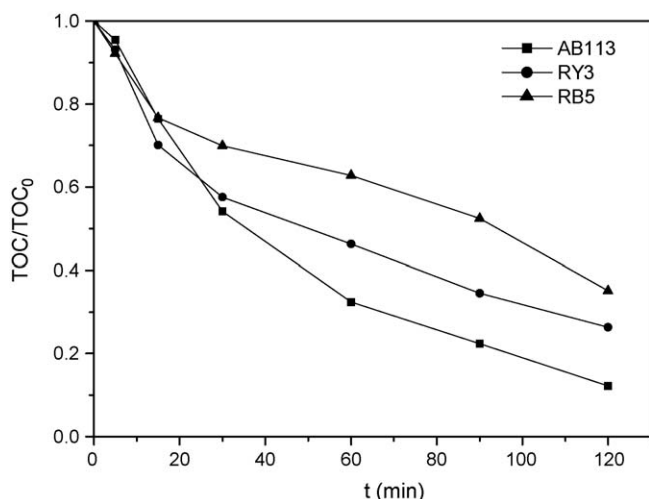


Fig. 4. Evolution of dimensionless TOC during non-catalytic ozonation of AB113, RY3 and RB5 at the natural pH of the solutions ($C_0 = 50$ mg/L).

the intermediates obtained from the oxidation of the selected reactive dyes were more refractory to single ozonation than those corresponding to the acid dye, as shown in Fig. 4. The most refractory to mineralisation is the RB5 dye, which belongs to the anthraquinone class.

The ozonation of aromatic compounds usually leads to the formation of numerous intermediate such as aldehydes, ketones and carboxylic acids that tend to accumulate in solution due to their low reactivity towards ozone [30]. Such compounds may be oxidized by secondary oxidants, such as hydroxyl radicals, produced during the decomposition of ozone in aqueous solution [8]. In the scope of heterogeneous catalytic ozonation, refractory compounds are mineralised by the transformation of ozone into more reactive species and/or by adsorption and reaction of the pollutants on the surface of the catalyst [9].

Even though the decolourisation of the synthetic coloured solutions was not visibly enhanced by the studied catalytic systems, entirely different results were observed when analyzing the extent of the mineralisation achieved during catalytic ozonation. The kinetic data corresponding to the evolution of TOC during the catalytic ozonation of AB113, RY3 and RB5 are presented in Figs. 5–7, respectively.

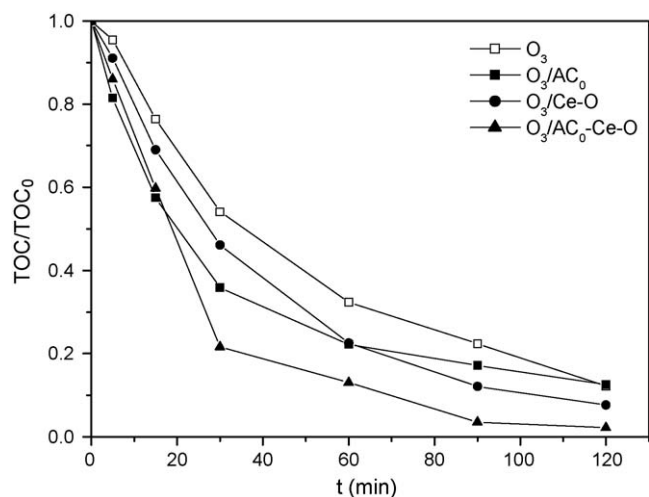


Fig. 5. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of AB113 ($C_0 = 50$ mg/L, pH = 5.8).

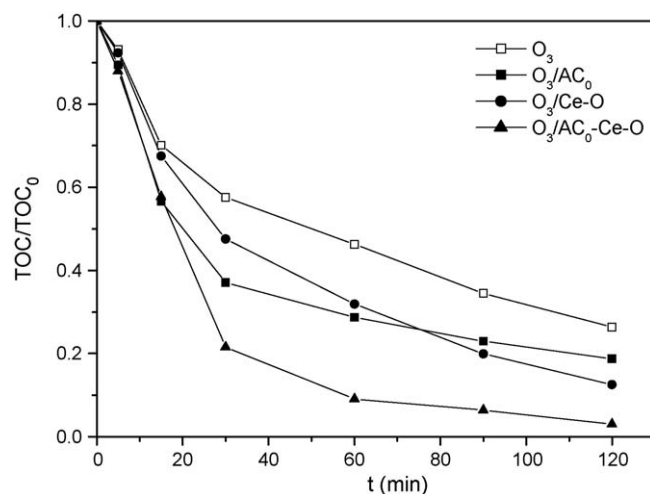


Fig. 6. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RY3 ($C_0 = 50$ mg/L, pH = 5.8).

The acid dye AB113 was found to be the less refractory compound among the studied dyes. Non-catalytic ozonation allowed the removal of 88% of TOC within 120 min of reaction. Nonetheless, the mineralisation of the solution was visibly enhanced by all the catalytic systems, as shown in Fig. 5. Activated carbon accelerated the mineralisation of the solution, yet the TOC removal rate seems to decrease after 60 min of reaction. Cerium oxide was shown to be active and the best results were achieved with the AC₀-Ce-O composite. Up to the first 15 min of reaction, the results obtained with AC₀ and AC₀-Ce-O were very similar. After that period there was a significant improvement in the removal of TOC obtained with the composite, leading to a higher mineralisation degree.

A very similar trend was observed for all the studied dyes. In the case of RY3 the simultaneous use of ozone and activated carbon led to an enhanced TOC removal when compared to single ozonation (Fig. 6). As previously shown, RY3 has very little affinity towards activated carbon; therefore, the enhanced results may be attributed to the catalytic effect of activated carbon mainly in the oxidation of intermediate products.

Comparatively to non-catalytic ozonation, the simultaneous use of ozone and activated carbon promoted increased the TOC

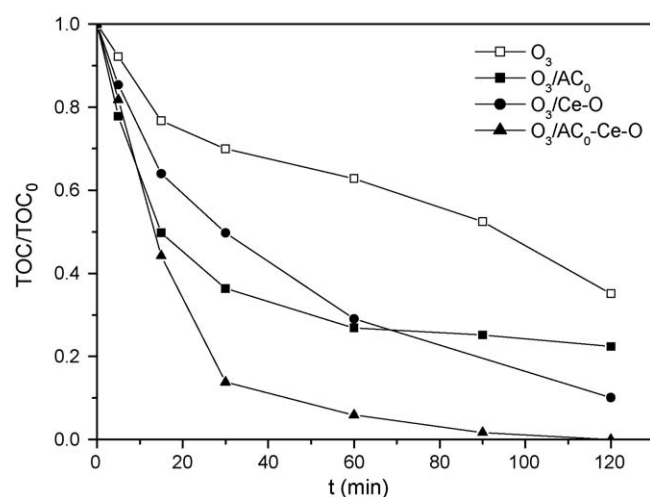


Fig. 7. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RB5 ($C_0 = 50$ mg/L, pH = 5.6).

removal from 42% to 63%, after 30 min. Also in this case, the highest mineralisation extent was obtained with the activated carbon–ceria composite. After 30 min of reaction, the TOC removal achieved was 78% against 42% obtained by single ozonation. Sample AC₀-Ce-O allowed nearly total mineralisation of the solution after a longer reaction period.

The reactive blue dye RB5 was shown to be the most refractory towards single ozonation and the biggest differences between non-catalytic and catalytic ozonation were observed in this case (Fig. 7). After 30 min of reaction, the mineralisation extent obtained in non-catalytic ozonation was only about 30%. The addition of the activated carbon to the process approximately doubled the percentage of TOC removed. A remarkable enhancement in the mineralisation degree is obtained during the ozonation catalysed by the composite AC₀-Ce-O. After 30 min, less than 14% of the initial TOC is present in solution and total mineralisation is achieved in less than 2 h of reaction. Cyclic experiments in the ozonation of dye RB5 were carried out reusing the sample AC₀-Ce-O, and it was observed that after 3 cycles the activity of the catalyst remains unchanged, within the experimental error, which is an evidence of its stability.

In all cases, cerium oxide was found to be an efficient ozonation catalyst and higher mineralisation degrees were achieved comparatively to the performance of activated carbon, but only for longer reaction periods (higher than ca. 60 min). Superior initial reaction rates are observed for the TOC removal during ozonation catalysed by both AC₀ and AC₀-Ce-O. This observation suggests a reaction mechanism distinct from that of cerium oxide catalytic ozonation. The latter is dependent on the formation of HO• radicals [25], while the former mainly comprises surface reactions on the activated carbon, as reported in a previous work [23].

During single ozonation, the pH of the solutions drops to a value between 3.5 and 4, which is explained by the formation of by-products of acidic nature, such as small chain carboxylic acids. In the presence of the composite AC₀-Ce-O, the final pH of the solutions is usually higher, especially in the cases of AB113 (pH 5.8) and RB5 (pH 5.1), approximating the pH values of the initial solutions. These observations together with the TOC measurement confirm a highly efficient elimination of most of the oxidation by-products.

Previously, it was observed that the three dyes behaved in a different way towards non-catalytic ozonation, being RB5 the most refractory compound. When comparing the results obtained during catalytic ozonation, different conclusions were withdrawn. No major differences were observed in terms of TOC removal among the three catalysts used. In fact, for the most promising catalytic system O₃/AC₀-Ce-O, a slightly faster mineralisation was observed for the anthraquinone dye, which is probably related to the nature of the intermediates formed. Even though those are resistant to ozone attack, they are mineralised during catalytic ozonation, due to the existence of less selective and highly oxidant species, as is the case of HO• radicals, and to the catalytic oxidation occurring on the surface of the composite. These observations suggest that the results obtained with the catalytic ozonation systems are less influenced by the type of the coloured solutions than non-catalytic ozonation.

3.1.1. Effect of dye concentration in the catalytic ozonation of Reactive Blue 5

Depending on the type of dyes and dyeing processes used, dye concentrations of 0.01 g/L up to 0.25 g/L have been cited as being present in dyehouse effluents [26]. Reactive dyes have fairly low fixation levels, which may vary in the range of 50–90%, resulting in strongly coloured spent dyebaths. In spite of the deep colouration caused by very small concentrations of dyes, their contribution to

the organic content of the solution is relatively low. In this work, the initial TOC content of the 50 mg/L solutions of the selected dyes was within 11–17 mgC/L. In order to study the influence of the concentration of dye in the ozonation process, a solution of 300 mg/L of RB5, with a corresponding TOC of 66 mgC/L, was prepared.

Both single ozonation and ozonation catalysed by AC₀, Ce-O and AC₀-Ce-O were carried out. The evolution of the UV–vis spectra was recorded along time, and the colour of the solution was assessed at 598 nm. With the increase in the concentration of the reactive dye from 50 to 300 mg/L, the time required for nearly complete decolourisation increased from 10 to ca. 30 min (results not shown).

The experimental curves corresponding to the removal of TOC during non-catalytic and catalytic ozonation of the 300 mg/L RB5 solution are depicted in Fig. 8. As expected, as the initial dye concentration increased, the extent of mineralisation of the RB5 solution decreased (cf. Fig. 7).

After 15 min of single ozonation 91% of initial colour was removed, although total decolourisation was only achieved after approximately 30 min of ozonation. Nonetheless, after this period of ozonation, only 16% of the TOC was removed. Cerium oxide had no visible activity up to this point of the reaction. Additionally, no major differences were observed between the performance of AC₀ and AC₀-Ce-O during this period. A distinct effect in the catalysts activity was more pronounced after the total decolourisation period (ca. 30 min). According to Fig. 8, after 120 min of reaction, the activated carbon promoted ozonation increased TOC removal from 48% (obtained with non-catalytic ozonation) to 66%. Cerium oxide allowed a TOC removal of 69% and, for longer reaction times, better results were obtained comparatively to the performance of activated carbon alone. Similarly to what had been observed for the experiments with the lower dye concentration, the highest mineralisation degree was obtained with the AC₀-Ce-O composite. After an initial period, where the composite behaves likewise the activated carbon, the ozonation catalysed by the composite leads to an enhanced mineralisation extent, which is mostly due to the formation of HO• radicals that are responsible for the mineralisation of the oxidation products. In fact, this period is coincident with that observed when comparing non-catalytic ozonation and ozonation catalysed by Ce-O, where a significant catalytic effect starts to be observed after 30 min of reaction. A mineralisation degree of 85% is achieved after 120 min of reaction with AC₀-Ce-O, which is 1.8 times the value obtained with non-catalytic ozonation.

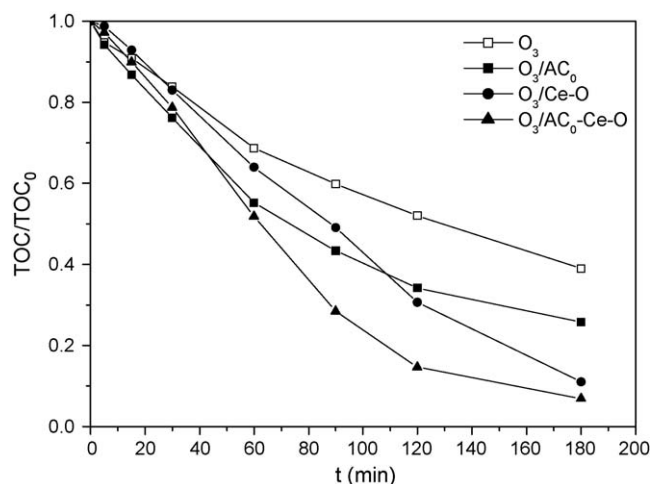


Fig. 8. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of RB5 ($C_0 = 300$ mg/L, $pH = 5.6$).

Even though there is no experimental data concerning the concentration of dissolved ozone, it is believed that, in an early stage of the reaction, ozone is mainly consumed in the destruction of the chromophores of the dye molecules, and in the degradation of aromatic moieties and unsaturated compounds. As the refractory character of the solution increases, ozone is transformed into HO^\bullet radicals that are responsible for the mineralisation of most of the compounds in solution. Simultaneously, oxidation of some of those products occurs on the surface of the activated carbon through a mechanism that involves, not only HO^\bullet radicals, but also surface oxygenated radicals resultant from the reaction between ozone and activated carbon [23,31].

Some selected samples collected during the ozonation experiments were analyzed by HPLC in order to evaluate the nature of the intermediate compounds. Due to the complexity of the dye molecule and to the large number of possible oxidation by-products, the HPLC analysis was focussed on the samples collected at longer reaction times (60, 120, 180 min). The intermediates and final products of the dyes ozonation reaction depend on their chemical structure. According to the literature [32,33], aromatic amines, phenols, quinones, hydroquinones, phthalic, muconic, fumaric, maleic acids, etc. have been identified among the oxidation by-products generated. However, all of these by-products are detected at the early stages of ozonation and disappear completely for longer reaction periods. On the other hand, sulfate ions, nitrate ions, nitrogen, oxalic, formic and acetic acids are usually identified as final accumulated products. In this work, the qualitative evaluation of the chromatograms allowed the identification of carboxylic acids (oxalic and oxamic acid), which are responsible for a fraction of the TOC in solution. Nitrates were also detected in small concentrations. Sample $\text{AC}_0\text{-Ce-O}$ led to nearly total mineralisation of the oxalic acid. Oxamic acid was produced in much lower concentrations than oxalic acid. Due to its extreme refractory character [23,34] it was only partially removed from solution, being the lowest concentration detected for the O_3/AC_0 system. The concentration of nitrates was lower whenever either AC_0 or $\text{AC}_0\text{-Ce-O}$ was used. These observations are in agreement with our previous findings related to the catalytic ozonation of several aromatic compounds and carboxylic acids [23,35].

3.1.2. Effect of the presence of carbonates and bicarbonates in the ozonation of CI Reactive Blue 5

Generally, in addition to dyes, reactive dye baths involve the use of several auxiliary chemicals, such as sodium chloride (NaCl), sodium carbonate (Na_2CO_3), also known as soda ash, and sequestering agents. In this section, the influence of the addition of Na_2CO_3 in the catalytic ozonation of dye solutions is assessed. The main role of the Na_2CO_3 is to increase and buffer the pH of the dye bath, favouring the reaction between the reactive group of the dye and the $-\text{OH}$ groups of the cellulose.

The presence of inorganic ions such as carbonates and bicarbonates may affect the destruction of organic compounds in water and wastewater through advanced oxidation processes. Carbonate (CO_3^{2-}) and bicarbonate ions (HCO_3^-) are well known as hydroxyl radical scavengers. Both species react with hydroxyl radicals to produce carbonate radical ions via the following reactions [36], respectively at moderate and high pH levels:



As demonstrated by the rate constants, carbonate ions are much stronger scavengers than bicarbonate ions. Therefore, in relation to the subject under discussion, the bicarbonate concentration

eventually present in an ozone wastewater treatment process is less important than the concentration of carbonate.

The characterization of a textile effluent representative of a global effluent collected after a conventional activated sludge biological treatment, revealed a concentration of inorganic carbon (IC) of ca. 100 mgC/L, which is due to the presence of HCO_3^- and CO_3^{2-} .

Assuming that this content results mainly from the addition of Na_2CO_3 during the dyeing step, a concentration of approximately 1 g/L was estimated and used in the simulated coloured effluent. The addition of 1 g/L of Na_2CO_3 to the 300 mg/L RB5 solution led to a significant pH increase from ca. 5.6 to 11.5, which corresponds to the typical pH of a reactive dyeing bath. However, in order to meet the conditions usually found in real textile effluents after biological treatment, the pH of the solution was adjusted to 8.5 by the addition of HCl solution. At this pH the equilibrium of the HCO_3^- and CO_3^{2-} species is shifted towards the formation of HCO_3^- , as only ca. 1% of the acid is deprotonated ($\text{pK}_a [\text{HCO}_3^-/\text{CO}_3^{2-}] = 10.4$).

The simulated effluent was treated by catalytic and non-catalytic ozonation. Both colour and TOC removal were measured along time. With the exception of the system O_3/AC_0 , which allowed a slightly faster colour removal, the decolourisation of the CI RB5 solution was not significantly enhanced during the catalytic ozonation (results not shown). Apparently, the rate of decolourisation seems to be slightly higher in this case, comparatively to the results obtained in the absence of carbonate species, which may be related to the solution pH (8.5 vs 5.3). After 15 min of reaction, the colour removal lies between 97% and 98% for all the catalytic systems and the time required for nearly total decolourisation was less than 30 min. The effect of the addition of sodium carbonate was mostly noticeable in the extent of the mineralisation of the solution. Experimental data referring to the TOC removal in all the studied systems is depicted in Fig. 9.

The results obtained by single ozonation are not significantly affected by the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ (cf. Fig. 8). Additionally, the catalytic action of AC_0 is only slightly affected, if compared with the results obtained in the absence of Na_2CO_3 . On the contrary, those anionic species were found to strongly inhibit the activity of both Ce-O and $\text{AC}_0\text{-Ce-O}$. As previously mentioned, the addition of Na_2CO_3 increases the solution pH and alkalinity. The mineralisation of organic compounds, achieved by ozonation, is usually favoured at higher pH values, due to the participation of HO^\bullet radicals in the reaction mechanism. However, the scavenging effect of both HCO_3^- and CO_3^{2-} species decreases the amount of

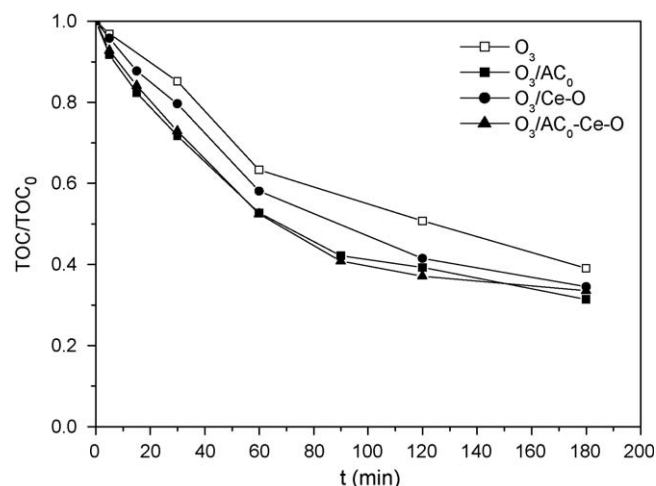


Fig. 9. Effect of the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in the mineralisation of RB5 ($\text{C}_0 = 300 \text{ mg/L}$, $\text{pH} = 8.5$).

HO• radicals available for reaction with the organic compounds, therefore inhibiting the mineralisation process. In a previous work [25], cerium oxide was shown to catalyse the ozonation of carboxylic acids mainly through the reactions involving HO• radicals. In the present work, the inhibiting effect of the $\text{HCO}_3^-/\text{CO}_3^{2-}$ confirms that the mineralisation of the intermediates of the process also occurs through a radical mediated reaction mechanism. Nevertheless, Ce-O still has a significant catalytic activity, as higher mineralisation is attained when compared to single ozonation. In the case of the composite, the results obtained up to 60 min of reaction are not particularly affected by the presence of the sodium carbonate (compare Figs. 8 and 9). After this period, a significant reduction in the catalyst activity was observed. The removal of TOC obtained after 120 min of reaction was 63% contrasting with the 85% obtained in the absence of carbonates.

The similarity of the performance of AC_0 and $\text{AC}_0\text{-Ce-O}$ in the mineralisation of the CI RB5 should be pointed out. Apparently, the presence of the scavenger has very little effect on the activity of the activated carbon, since only a slight reduction in the removal of TOC was observed for longer reaction period comparatively to the results obtained in the absence of the carbonates. This observation suggests that the contribution to the production of HO• radicals is not the only role of activated carbon. It is thought that activated carbon also promotes the decomposition of dissolved ozone that may originate surface oxygen-containing radical species, which participate in the oxidation of the organic compounds. In this way, activated carbon seems to be a good catalyst for practical purposes, as its activity is not significantly affected by the presence of HO• scavenging species.

3.2. Case study: catalytic ozonation applied to the treatment of textile effluents

Catalytic ozonation is a powerful chemical oxidation process that can be applied to the treatment of a vast range of organic pollutants, and it has been shown to be a promising technique to the treatment of wastewater from the textile industry. Due to its high decolourisation efficiency and extensive elimination of organic content, catalytic ozonation can be used as a final refining treatment in order to allow an eventual reutilisation of water.

In order to evaluate the efficiency of the selected catalysts in the ozonation of real wastewater samples, liquid effluents originated in textile plants were assessed. In this context, a mixed textile effluent collected after biological treatment (TEA) and a raw textile wastewater (TEB) were used as case studies. Some characterization parameters are listed in Table 2.

Textile effluent A (TEA) was collected in a collective wastewater plant, after conventional activated sludge treatment, but before the

subsequent physico-chemical step. It is a mixture of effluents from different textile plants and includes a fraction of domestic wastewater. Therefore it is representative of a global bio-treated textile wastewater. This sample presented a strong red colouration and very few suspended solids. The UV-vis spectrum of the effluent is depicted in Fig. 10. The effluent was filtrated under vacuum before use.

Experiments of non-catalytic ozonation and ozonation catalysed by AC_0 , Ce-O and $\text{AC}_0\text{-Ce-O}$ were carried out under the same conditions used for the synthetic coloured solutions. Despite the strong visible colour of the effluent, complete decolourisation was achieved by single ozonation shortly after 5 min (Fig. 10), confirming the strong decolourisation potential of ozone. In terms of colour removal, no significant improvement is obtained with catalytic ozonation (results not shown).

Nevertheless, the mineralisation of the solution was negligible after 5 min of ozonation (less than 4% of TOC removal), bearing out that the decolourisation is not directly related to mineralisation extent. The evolution in the mineralisation degree of the effluent, achieved by the different catalytic systems is depicted in Fig. 11, and compared to that obtained with non-catalytic ozonation.

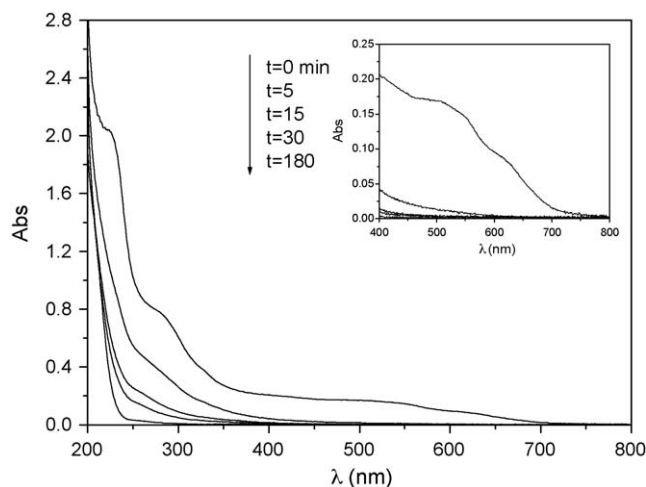


Fig. 10. Evolution of the UV-vis spectrum of TEA during non-catalytic ozonation (inset: magnification of the visible region of the spectrum).

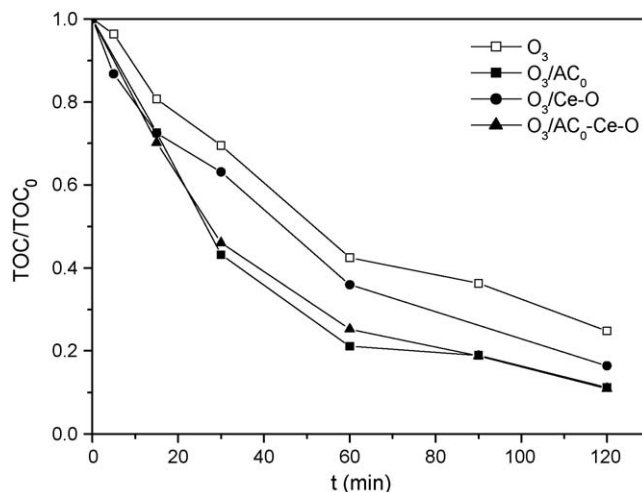


Fig. 11. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of TEA.

Table 2
Parameters of the industrial textile effluents selected.

	Textile effluent	
	Effluent A (TEA)	Effluent B (TEB)
Origin	Mixed with domestic sewage and collected after bio-treatment	Raw effluent
pH	8.3	9.3
TOC (mgC/L)	27	150
IC (mgC/L)	108	57
Conductivity (mS/cm)	2.84	3.11
Colour	Reddish-brown	Strong blue
Abs (436 nm) ^a	0.186	0.307
Abs (525 nm) ^a	0.160	0.230
Abs (620 nm) ^a	0.084	0.282

^a λ Defined by ISO7887:1994 for the determination of colour in real samples.

Under the selected experimental conditions the effluent seems to be easily mineralised by non-catalytic ozonation, with a TOC removal of 75% being achieved after 120 min. Nonetheless, a higher mineralisation degree was achieved with catalytic ozonation, being AC_0 and $\text{AC}_0\text{-Ce-O}$ the catalysts leading to the best results. In the presence of activated carbon, the removal of TOC achieved after 30 min was approximately 57%, which is significantly higher when compared to the 30% TOC removal achieved in non-catalytic ozonation. Unlike what was observed for all the studied dye solutions, no major differences were observed between activated carbon and the composite. Additionally, sample Ce-O was visibly less active. The performance observed during the catalytic ozonation of the bio-treated effluent was attributed to the presence of HCO_3^- and CO_3^{2-} , which, as explained in the previous section, act as radical scavengers, therefore inhibiting the mineralisation of the organic compounds via HO^\bullet oxidation. AC_0 and $\text{AC}_0\text{-Ce-O}$ have similar catalytic activities, which may be explained by the contribution of the surface reactions that are believed to occur preferentially on the activated carbon, therefore not involving HO^\bullet radicals in solution.

Textile effluent B (TEB) is a raw effluent collected in the equalisation tank of a wastewater treatment plant of a textile dyeing mill. Consequently, this wastewater is strongly coloured, and presents a relatively high organic load. Other characterization parameters are summarised in Table 2. Due to the presence of suspended solids, the effluent was filtrated under vacuum before ozonation experiments. Following the same approach of the rest of this work, effluent TEB was ozonised in the presence of AC_0 , Ce-O and $\text{AC}_0\text{-Ce-O}$, and the results were compared to those obtained with non-catalytic ozonation.

According to Fig. 12, the ozonation time required for nearly total decolourisation is approximately 30 min.

Due to the high organic content of this effluent, the degree of mineralisation attained with single ozonation is quite low. Despite the effective decolourisation obtained, the TOC removal achieved after 30 min of ozonation was approximately only 6%. Longer reaction times lead to higher mineralisation levels. However, after 180 min of ozonation only 44% of the organic content was removed, as shown in Fig. 13.

All the tested catalysts led to higher mineralisation levels, when compared to single ozonation. In this case, after 180 min of reaction best results were achieved with activated carbon, which allowed a TOC removal of 54%. Observing the experimental curves, and considering the amount of organic matter still present in

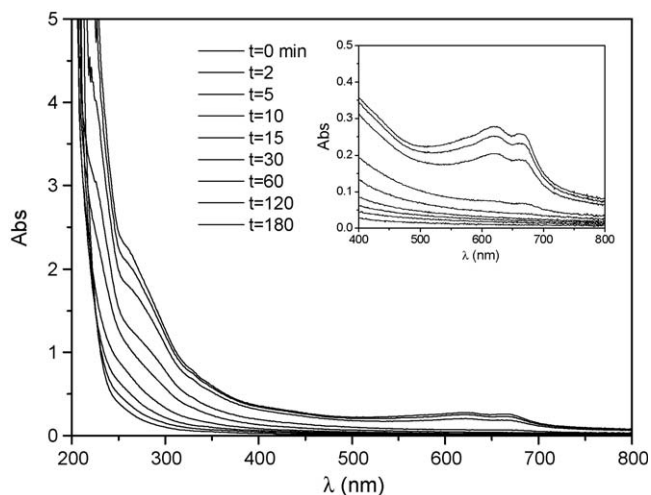


Fig. 12. Evolution of the UV-vis spectrum of TEB during non-catalytic ozonation (inset: magnification of the visible region of the spectrum).

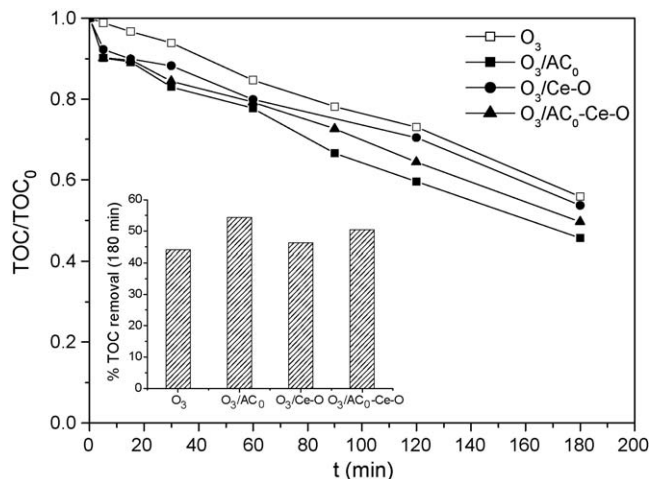


Fig. 13. Evolution of dimensionless TOC during non-catalytic and catalytic ozonation of TEB (inset: % TOC removal achieved after 180 min).

solution after 180 min, it seems that, even longer reaction times, and consequently, higher ozone doses would be necessary to accomplish total mineralisation. When comparing the concentration of ozone in the gas phase at the outlet of the reactor, it is obvious that the consumption of ozone was much higher for TEB, comparatively to TEA, which is related to the nature and the concentration of the dissolved organic compounds.

According to the literature [3], and to the present results, ozonation is not suitable to be used as a main wastewater treatment. Conversely, the application of ozone processes as post-treatment for a refined depuration of wastewater is of great interest. In the case of liquid effluents from the textile industry, ozone has proven to be highly effective for an extensive elimination of colour. Concerning the removal of recalcitrant compounds, which cannot be eliminated in biological processes, catalytic ozonation emerges as a feasible solution to significantly enhance the mineralisation of such effluents.

3.3. Reaction pathways involved in the catalytic ozonation

The scheme presented in Fig. 14 illustrates the main possible reaction pathways occurring in the ozonation of dyes (and other organic compounds) catalysed by the ceria-activated carbon composite.

Activated carbon is known to promote ozonation reactions. According to the results presented in this study and in the literature, activated carbon is believed to promote the decomposition of ozone into HO^\bullet radicals. Simultaneously, it is known that activated carbon catalyses the ozonation of organic species possibly by a surface mechanism that does not involve HO^\bullet radicals as the main oxidant species, as reported elsewhere [23]. In another work [25], cerium oxide was found to catalyse the decomposition of oxalic acid, mainly by the transformation of ozone into HO^\bullet radicals that would further react in the liquid phase. A noteworthy synergistic effect arose from the intimate mixture of ceria and activated carbon. It was assumed that the existence of delocalized electrons on the basal planes of the activated carbon contributes to the formation of Ce (III) species, which are thought to be necessary for promoting the decomposition of O_3 into HO^\bullet radicals by redox reactions on the catalyst surface involving the pair Ce (III)/Ce (IV).

In summary, the mechanism of the ozonation catalysed by the ceria-activated carbon composite is believed to comprise both surface reactions, similar to what occurs with activated carbon promoted ozonation, and also liquid bulk reactions involving HO^\bullet

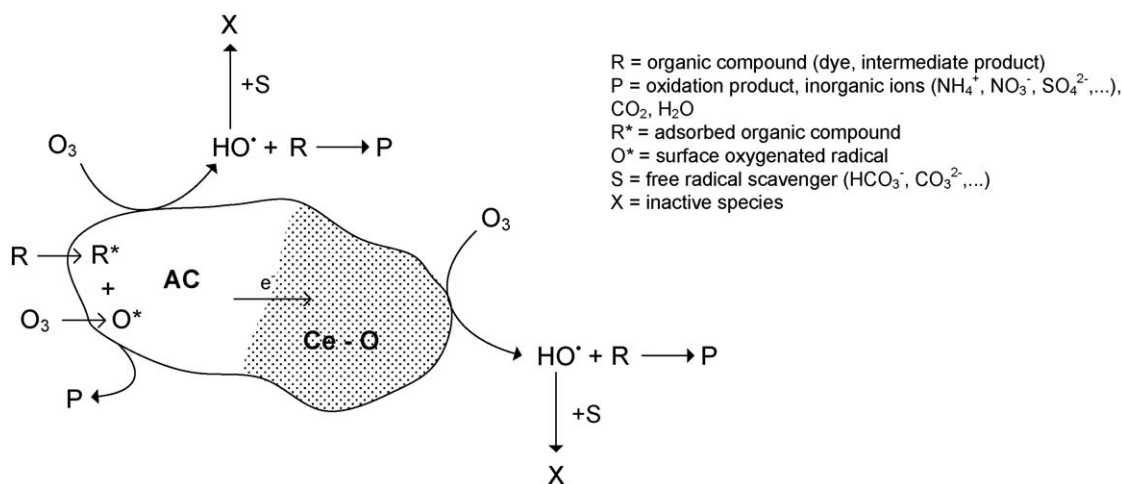


Fig. 14. Illustrative representation of the main reaction pathways occurring during ozonation catalysed by $\text{AC}_0\text{-Ce-O}$.

radicals, resultant from the catalytic decomposition of ozone on the surface of the catalyst.

4. Conclusions

The present study reports experimental kinetic data on the colour removal and mineralisation of CI Acid Blue 113, CI Reactive Yellow 3 and CI Reactive Blue 5 solutions, and two different textile effluents. Ozonation is a powerful oxidation process for fast and total decolourisation of both synthetic dye solutions and real textile effluents. Catalytic ozonation notably enhanced the mineralisation of the dye solutions. However, no major improvements were observed in the rates of colour removal. Such results are explained by the high decolourisation potential of ozone.

Within the experimental conditions settled for this work, adsorption in activated carbon was not efficient enough for the decolourisation of the dye solutions. The combination of activated carbon with ozone enhanced the mineralisation levels of both the dye solutions and the textile effluents.

The results obtained in this study show that cerium oxide catalysts is an effective ozonation catalyst for the mineralisation of textile dyes. Comparatively to the performance of the commercial activated carbon, an enhanced mineralisation extent was achieved, which is explained by a higher ability to catalyse the decomposition of ozone into HO^\bullet radicals. A strong synergic effect was observed between activated carbon and cerium oxide in the prepared composite, leading to enhanced mineralisation degrees for all the studied dye solutions.

The presence of bicarbonate and carbonate ions in solution was shown to partially inhibit the mineralisation of the CI Reactive Blue 5 dye. The negative impact on both Ce-O and $\text{AC}_0\text{-Ce-O}$ activities is supposed to be related to the scavenging effect of those inorganic ions on the HO^\bullet radicals formed. The presence of high concentrations of inorganic ions with scavenging properties may restrain the results obtained in wastewater treatment by advanced oxidation processes. Activated carbon catalysts also promote surface oxidation reactions that do not involve HO^\bullet radicals in solution; therefore their activity is not severely affected by the presence of scavenger species. This was confirmed by testing the efficiency of these catalytic systems in the mineralisation of real textile effluents. Ozonation processes are not suitable to be used as main wastewater treatments. However, they are attractive alternatives

to conventional physical-chemical processes, as tertiary treatments for bio-treated effluents.

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